Synthesis of a Novel 2D Lead Halide Perovskite to Uncover Structure-Property Relationships

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Concepts & Goals

This project is centered around $(CMA)_2(FA)Pb_2Br_7$. Previous work[1] has established a trend between structure and optical properties for a general form of 2D iodide perovskites. Understanding that relationship led the team to develop $(CMA)_2(FA)Pb_2I_7$ whose structure was tuned to achieve beneficial optical properties. This project seeks to understand how the relationship might extend to bromide materials.

	Formula	n=	Dimensionality
General	$(CMA)_2(FA)_{n-1}Pb_nX_{3n+1}$	n	2D or 3D
113	$(FA)PbX_3$	∞	3D
2127	$(CMA)_2(FA)Pb_2X_7$	2	2D
214	$(CMA)_2PbX_4$	1	2D

$(CMA) = C_7H_{15}N$,
$(FA) = CH_5N_2$

Table 1: Shows the family of materials that make up this specific form of 2D PbX perovskite. The n=2 is specifically studied, but the others show up as impurities. Note that n describes the number of layers of inorganic octahedra.

Most of the work on this project has been optimizing synthesis for purity to allow for clean optical measurements. 2127 contains all the parts needed to make 113 and 214, thus making a pure synthesis difficult.

Exciton interactions largely control optical properties for this material and similar materials. Exciton binding energy is high due to dielectric confinement from the wide organic layer (made of (CMA) in this case) and distortion in the octahedra.

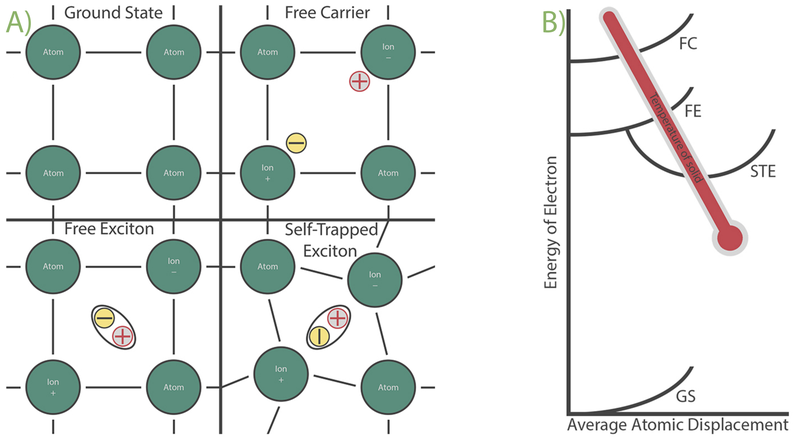


Figure 1: A) (left) There are four states an electron may be in. Note that each step brings charged particles towards their opposites. B) (right) Following this pattern, GS (ground state) and STE (self-trapped exciton) have the lowest energy. With an increase in temperature (thermal energy) higher energy states become more common.

Synthesis & Identification

Purity is achievable in two ways. Saturation testing alters molarity and cooling to control crystal growth. This creates large and pure crystals with seperable species. Molar testing alters molar ratios. This stops impurities from forming.

Saturation Testing

	Species	Variation	Cooling
Sample A	2127	Control	N/A*
Sample B	2127	Control	10°C/hr
Sample C	214	Lower Molarity	10°C/hr
Sample D	214	Lowest Molarity	N/A*

Table 2: shows the output species of four different samples, how their materials were altered, and how they were cooled. *This sample cooled naturally

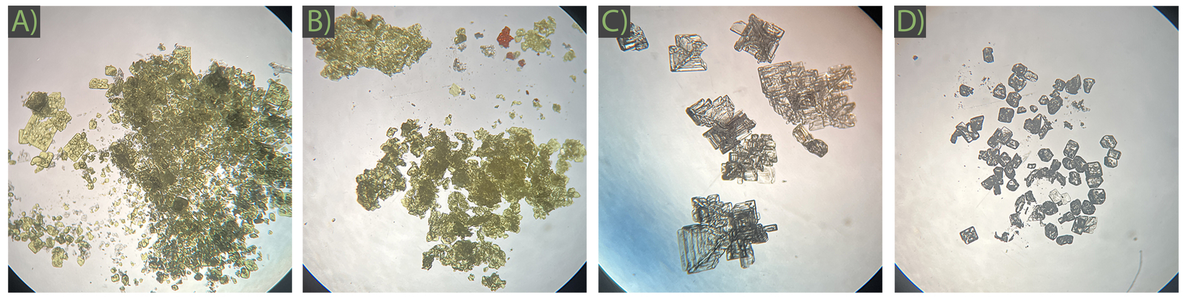


Figure 3: A) Sample A, yellow 2127 crystals, with small plate-like crystals. B) Sample B, 2127 crystals, with smaller, deeply intergrown plate-like crystals. C) Sample C, clear 214 crystals, larger and made of intersecting planes. D) Sample D, 214 crystals with thick, almost cubic shape.

The samples show progress toward separability. A is 2127 single crystals, C is large, and D is thick. However, A is too small, B and C have great intergrowth, and C and D are pure 214. This is likely due to (FA)'s high solubility causing it to remain in solution.

Separation can be done because 2127 is yellow, 113 is red, and 214 is clear.

Molar Testing

Tracking impurity presence is done using PXRD (Fig 4). (FA) molarity has a negative relation with 214 population. The position of the 113 peaks makes it difficult to identify small quantities of 113.

PXRD for Molar Testing

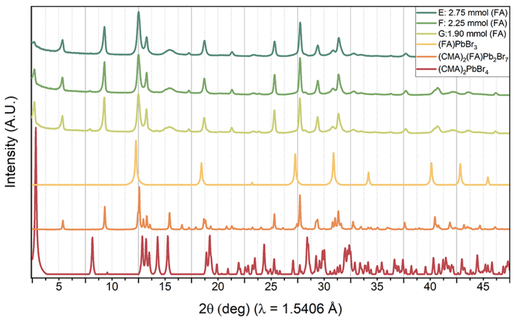
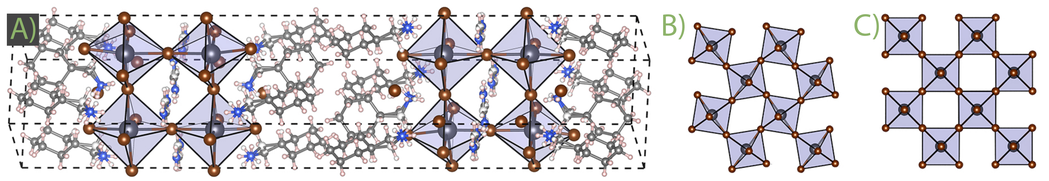


Figure 4: XRD Plot comparing PXRD patterns for molar testing samples and simulated patterns for (FA)PbBr3, (CMA)2PbBr4, and (CMA)2(FA)Pb2Br7.

Structural Analysis



	I	Br	% Dif.
Average Bond Length (Å)	3.194	3.005	5.921
Distortion Index	0.013	0.014	-7.578
Bond Angle Variance	11.738	10.427	11.169

Table 3: A selection of structural parameters showing how bond length changes, but doesn't cause a large change in distortion.

Figure 5: A) Two unit cells of 2127. There are two sections, an organic layer made of two (CMA) and an inorganic layer made of PbBr octahedra with (FA) in between the layers. B) & C) A comparison between the actual and idealized tiling of the octahedra.

The structures of the Br (Fig 5) and I variants are nearly identical. Octahedral tilting is prominent, but it is constant between the halides. The Br-Pb-Br bond length is smaller, but not small enough that the (FA) distorts the bond angle to a significant degree (Table 3). Then, the only parameter left is atomic radius, which shrinks, causing smaller bond length, more bond overlap, and finally a greater bandgap. Therefore, the Br material should have a greater self-trapped exciton population, consistent with the literature[2].

Further Work

Current work is mostly towards refining the synthesis process. This means increasing (FA) & lowering concentration, and, now knowing the approximate crystallization temperature a more informed cooling rate can be used. In the long term, writing has already begun, and deeper research into the structural dynamics of n=2 perovskites will soon begin.

References

1. Guo, S., et al. (2024). *Nat Commun*, **15**: 3001
2. Yakunin, S., et al. (2019). *Nat. Mater.* **18**: 846–852.

Acknowledgements

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